Low-Pressure Equation of State of Polymers

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The study of the dynamic deformation of polymers requires knowledge of the equation of state (EOS). Because polymers are often used in applications where the loading is either weak shock or nonshock, to model the thermo-mechanical response it is necessary to know the low-pressure EOS. Hugoniot shock data offers a standard means in the shock research community to determine the EOS but unfortunately Hugoniot data below one GPa is typically difficult to obtain with sufficient accuracy to be reliable. The objective here is to show that an alternative low-pressure EOS can be constructed by information that is either already in the published literature or is readily obtained by experiment. In the present work we consider two representative polymers: amorphous polycarbonate (PC) and semi-crystalline polytetrafluoroethylene (PTFE). PTFE is chosen to show that crystalline phases can be handled, at least approximately, by this simple semi-empirical method.

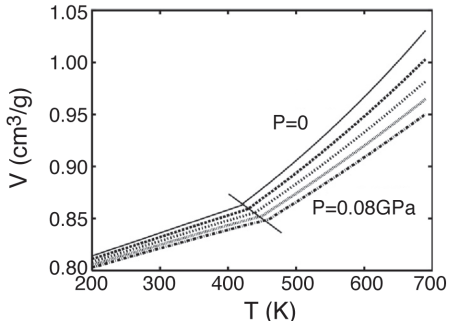


Fig. 1.
Specific volume for PC. The solid line is the glass transition boundary. Pressures correspond to 0.0, 0.2, 0.4, 0.6. and 0.8 GPa.

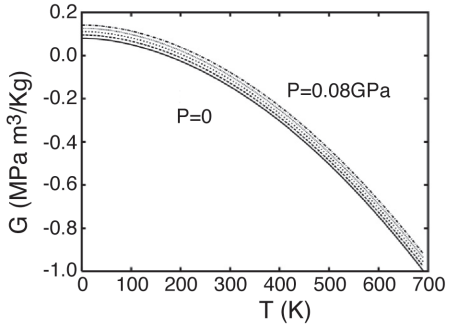
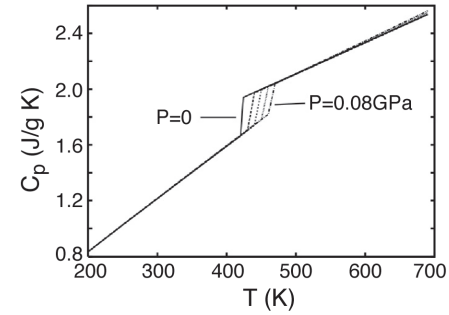
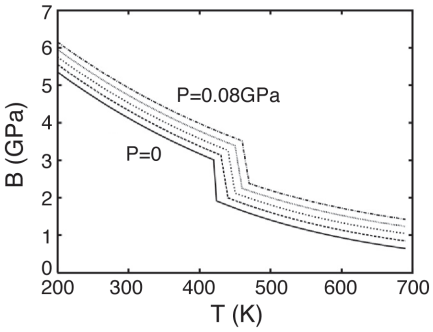


Fig. 2.
Gibbs free energy for PC. Pressures correspond to 0.0, 0.2, 0.4, 0.6. and 0.8 GPa.

The crystalline portion of PTFE, which makes up typically 30-70% of the total volume of the polymer, can exist in four low-pressure phases, three of which will be included in our analysis. Polycarbonate is glassy at room temperature and has a glass transition temperature near 150°C. The present analysis shows that the glass transition can be included in the EOS. Finally, it is emphasized that the present work uses standard techniques to obtain the Gibbs free energy from which the Hugoniot can be constructed and compared to the low-pressure experimental Hugoniot when it exists.

To construct the EOS, the Gibbs free energy is written as the sum of zero-pressure and a pressure-dependent term. The latter term is consistent with the Tait equation for the specific volume [1] and the zero-pressure terms are expressed as a polynomial in temperature plus a logarithmic contribution. For PC we use the specific volume data and analysis of Zoller [2] and the ambient pressure heat capacity data of Cheng and Wunderlich [3]. The coefficients to the logarithmic term and the power series are determined by fitting the heat capacity data, and ambient (approximated as zero) pressure Gibbs free energy of Cheng and Wunderlich [3]. Because heat capacity is discontinuous at the pressure and temperature-dependent glass transition we fit coefficients to the two different regimes ($T<T_g$ and $T<T_g$) of the heat capacity. The pressure-dependent contribution is determined by fitting the theoretical specific volume to the measured specific volume of Zoller [2]. The resulting specific volume and Gibbs free energy for PC are shown in Figs. 1 and 2, respectively. Taking the appropriate derivatives of the Gibbs free energy gets other thermodynamic quantities. For example, Figs. 3 and 4 show the specific heat at constant pressure and the isothermal bulk modulus. The glass transition is responsible for the pronounced jump occurring in these quantities.





The commonly used phase diagram [4] for PTFE is shown in Fig. 5. The crystalline phases for PTFE exist in four low-pressure crystalline structures labeled Phase I through IV. Glass transitions, related to the amorphous phase, also occur in PTFE at temperatures outside the range of the phase transitions. Phase IV will be ignored in our work because its properties are intermediate between Phases I and II. We will also ignore the glass transitions. Consequently, the resulting EOS described here will be valid for temperatures between approximately 250 K and 380 K, and pressure below 1 GPa. Using the specific volume data of Weir [5], the heat capacity data of Loufakis and Wunderlich [6], and the phase diagram, we have constructed the EOS for PTFE for Phases I, II, and III. Figure 6 shows the Gibbs free energy. The stable thermodynamic state is the one with the lowest Gibbs free energy and the crossing of the free energies determine the solid-solid phase boundaries. The dotted lines in Fig. 6 are our theoretical phase boundaries, as determined by the Gibbs free energy crossings and, when written in terms of pressure and temperature, can be compared favorably with the phase diagram of Fig. 5.

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[1] Tait, P. G., *Phys. Chem.* **2**, 1 (1888).
[2] Zoller, P., *J. Poly. Sci.: Part B: Polymer Phys. Eds.* **20** 1453 (1982).
[3] Cheng, S. Z., and Wunderlich, B., *J. Poly. Sci.: Part B: Polymer Phys. Eds.* **24** 1755 (1986).
[4] Beecroft, R. I., and Swenson, C. A., *J. Appl. Phys.* **30** 1793 (1959), (this work omitted Phase IV).
[5] Weir, C. E., *J. of Research. Natl. Bur. Standards* **53** 245 (1954).
[6] Loufakis K., and Wunderlich, B., *Polymer* **26** 1875 (1985).

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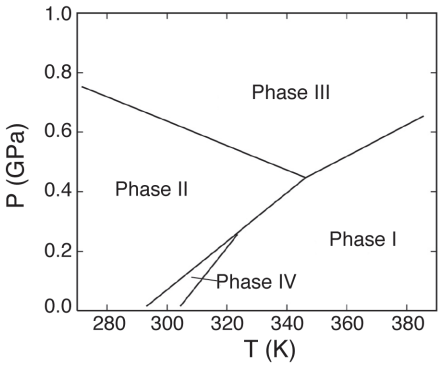

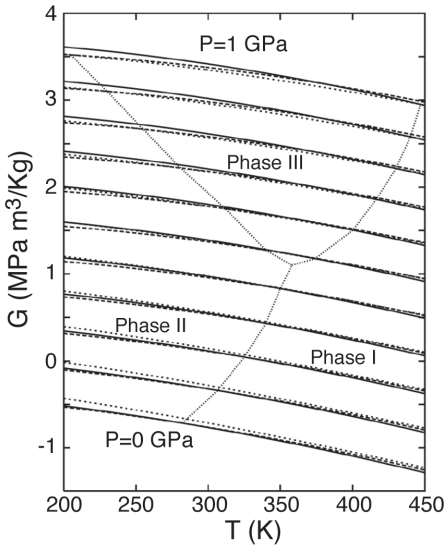

Fig. 3.
Constant pressure heat capacity for PC.

Fig. 4.
Isothermal bulk modulus for PC.

Fig. 5.
PTFE phase diagram.

Fig. 6.
Gibbs free energy for PTFE for Phase I, II, and III.